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(54) **A method for the production of HNS II.**

(57) The invention relates to a method for the production of a 2,2',4,4',6,6'-hexanitrostilbene (HNS) with specified purity and bulk density, generally referred to as HNS II, from a less pure raw-product with lower bulk density, generally referred to as HNS I. According to the invention, the raw-product is purified through recrystallisation from a solvent, of which N-methylpyrrolidone gives by far the best result, while the bulk density of the product is increased by ultrasonically treating the resulting crystals, thereby decreasing their length to bredth ratio.

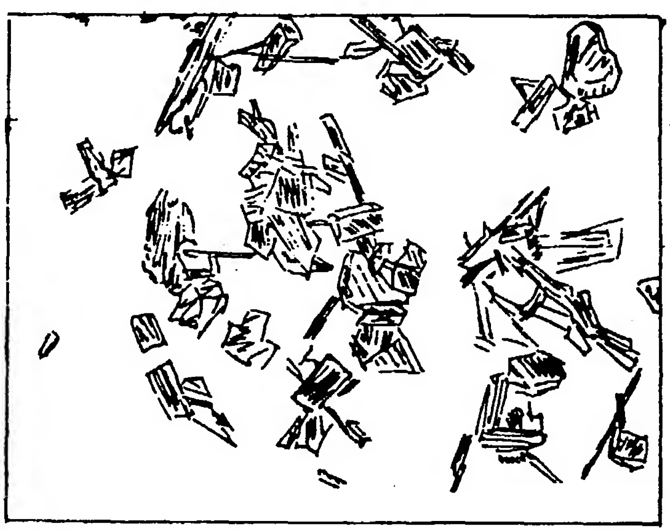

Fig. 2

A METHOD FOR THE PRODUCTION OF HNS II

This invention relates to a method for the production of HNS II, which is 2,2',4,4',6,6'-hexanitrostilbene (HNS) with specified purity, properties and bulk density, from a less pure raw-product, with lower bulk density, usually referred to as HNS I.

The search for explosives which retain their performance characteristics after being subjected to high temperatures for long periods, for use in for example space technology and natural oil-gas recovery, has focused to a large extent upon 2,2',4,4',6,6'-hexanitrostilbene (HNS) as a promising candidate. The purified explosive has a melting point of 319°C and exhibits virtually unchanged explosive properties after being heated at 232°C for 200h. Furthermore it is easily manufactured from the readily available 2,4,6-trinitrotoluene (TNT) according to the process described in US 3 505 413. The product so obtained, HNS I, is not however pure, containing small amounts of TNT, hexanitrobibenzyl, and other impurities, and consequently its properties are somewhat less than optimal. Its melting point is usually around 315°C and its thermal stability is significantly reduced from that of the purified explosive HNS II.

During the past 20 years considerable effort has been devoted to finding methods for purifying HNS I to the high quality HNS II, which has the specifications listed in Table 1. While several methods for purifying HNS I have now been published, many of them give HNS below the specification limits for HNS II in one or more respects. All of these methods involve either recrystallisation or digestion of the HNS I using either an organic solvent system or nitric acid, sometimes followed by physical processing of the crystals.

Since HNS has a rather low solubility in most organic solvents, the choice of solvents for recrystallisation is rather limited. Most work has focused on the use of dimethylformamide (DMF), 90% HNO_3, and to some extent acetonitrile. The use of DMF, alone or in conjunction with acetonitrile, gives HNS in the form of long needles with a rather low bulk density (0.25-0.45gcm^{-3}). However the handling characteristics can be improved by milling, the crystals being fractured and the bulk density increased to around 0.55gcm^{-3}. Unfortunately the main limitation of this method is the use of DMF as the solvent ; whilst most of the specification requirements for HNS II are satisfied, the use of DMF almost invariably leads to vacuum test results which exceed the specification limit (<0.6mlg^{-1} for 20min at 260°C; the value at 2h is usually within the specification limit). The use of digestion rather than recrystallisation is also only partially successful. Whilst most of the impurities are removed by this method, the bulk density cannot reliably be increased above 0.45gcm^{-3}. Recrystallisation from 90% HNO_3 is widely used in the manufacture of HNS II because it is relatively cheap and easy to perform. However it is generally felt that the resulting product is almost always contaminated with nitric acid. E.E. Kilmer (NSWC/WOL TR 78-209; also 75-142) has made a thorough study of this question and demonstrated that HNO_3 can be effectively removed from the crystals by proper washing and drying (120°C in vacuo - not in air). He concludes however that fulfillment of the vacuum test requirements is much easier when organic solvents such as acetonitrile/toluene or acetonitrile/xylene are used. Kilmer also studied the performance of detonating cord filled with HNS II which had been recrystallised from either 90% HNO_3 or acetonitrile/toluene or acetonitrile/xylene, after thermal treatment at 218°C (425°F), or repeated cycling between -54°C (-65°F) and 177°C (350°F). With HNS II which contained as little as 0.01% residual HNO_3, he observed decreased detonation velocity after repeated thermal cycling, or even after normal storage for 4 years, and decreased detonation velocity (failure after 20h) and chemical degradation (<20% HNS remained after 20h) on heating at 218°C. By contrast, HNS II obtained by acetonitrile/toluene or acetonitrile/xylene recrystallisation, was resistent to themal treatment viz. no decrease in the detonation velocity was observed after 264h at 218°C, or after 100 thermal cycles.

The most satisfactory, reported method for producing HNS II with regard to product specification is that described by L.J. Syrop in US 3 699 176 and US 3 832 142. This consists of a continuous extraction process, in which hot acetonitrile extracts HNS from solid HNS I and this solution then passes into a higher boiling , non-solvent for HNS eg.toluene or xylene. The HNS thus separates from the boiling acetonitrile/toluene or acetonitrile/xylene mixture as HNS II, and the acetonitrile is returned to the extraction cycle. This method gives excellent HNS II with bulk density around 0.5gcm^{-3}, melting point 319°C, and good vacuum stability (260°C), but is rather slow due to the low solubility of HNS in acetonitrile.

The present invention avoids the deficiencies of the above reported methods for producing HNS II by (i) using N-methylpyrrolidone (1-methyl-2-pyrrolidone) as the recrystallising solvent, and (ii) using ultrasonic treatment to fracture the needle-shaped crystals, reducing their length-bredth ratio, and thus giving an increased bulk density. The resulting product satisfies all the specification limits for HNS II (see Table 1), and in addition has a particularly high bulk density, possesses excellent powder flow and handling characteristics, and retains essentially unchanged explosive properties after prolonged heat treatment. The bulk density was measured according to DIN 53 194. (A sample, which had a bulk density of 0.90gcm^{-3}

when measured according to DIN 53 194, had a bulk density of 0.71gcm^{3} when measured according to the military specification WS 5003F).

Ultrasonic treatment implies treatment with <u>sound</u> having a frequency above that which can be detected by the human ear i.e. > 16000-20000Hz.

<u>Table 1</u>

	HNS purified according to the invention	Starting HNS (HNS I)	Specification** for HNS II
Chemical analysis:			
Hexanitrobibenzyl (%)	<0.01	0.22	<1.2
2,4,6-Trinitrotoluene (%)	<0.01	0.01	-
Others (%)	undetectable	0.49	0.05
Surface moisture (wt%)	<0.01	-	<0.05
Solubility in water (wt%)	0.02	0.1-0.2	<0.03
Insoluble in DMF (wt%)	<0.01	0.05	<0.03
Acidity (ΔpH from control)	<-0.2	>-0.2	<-0.2
Bulk density (gcm^{-3})	0.81*	0.42*	>0.45
DSC max at $5^{o}min^{-1}$ (^{o}C)	320.5	317.5	m.p. 319
Vacuum stability (260^{o}C)			
1st 20min (mlg^{-1})	0.54	4.6	<0.6
additional 2h ($mlg^{-1}h^{-1}$)	0.41	2.4	<0.6

* according to DIN 53 194   ** according to WS 5003F

N-Methylpyrrolidone has previously been used by E.E. Gilbert as a solvent for the oxidation of hexanitrobibenzyl to HNS (Propellants and Explosives, 1980, <u>5</u>, 168; US 4 245 129; US 4 243 614; US 4 270 012; US 4 268 696), and for the conversion of TNT to hexanitrobibenzyl, replacing THF in the traditional Shipp-Kaplan process (Propellants and Explosives, 1980, <u>5</u>, 15), but its use as a recrystallising solvent for HNS has not been reported. Although quite structurally similar to DMF, N-methylpyrrolidone has almost twice the DMF-solvent capacity for HNS (solubility gHNS/100ml N-methylpyrrolidone : 4.3g at 10°C, 11.1g at 100°C, 17.8g at 125°C cf 6.1g HNS/100ml DMF at 100°C), and gives a product which has good vacuum stability at 260°C (see Table 1). The latter is the main limitation of DMF. The solubility data indicate that N-methylpyrrolidone should give recovery yields of 61% and 76% when saturated solutions of HNS are cooled from 100°C and 125°C resp. to 10°C. Example 1 indicates that recoveries close to the theoretical are readily attainable. Recovery yields can be increased further by the addition of a solubility reducing cosolvent such as chlorobenzene (Examples 2 and 3 ; 85.5 and 85% resp.) or toluene (Example 4; 82%), without raising the vacuum stability at 260°C above the specification limit.

The HNS obtained by recrystallistaion from N-methylpyrrolidone, with or without a cosolvent, is in the form of needles (see Fig 1) whose length to breadth ratio is dependent upon the temperature profile of the cooling cycle, and the rate of addition of the solubility reducing cosolvent when used. Typical bulk densities are 0.3-0.45gcm^{3}, with volume mean diameters (VMD) of 100-250μm. As such, the bulk density is below the specification limit for HNS II (< 0.45gcm^{3}), and the material has poor flow and handling characteristics. It has been discovered that the bulk density can be increased, accompanied by a decrease in VMD, and

the flow and handling characteristics greatly improved, by ultrasonic treatment of a suspension (slurry) of the recrystallised HNS.

Ultrasonic treatment of the recrystallised HNS may be performed as a batch process either in an ultrasonic bath or in a vessel fitted with a submersible ultrasonic generator, or as a continuous flow process using either a bath as the generator or a flow-through ultrasonic cell. The liquid in which the HNS is suspended (slurried) may be any chemically inert solvent system, but a largely aqueous medium is particularly effective (Examples 5-7). The mother liquor from the recrystallisation of HNS has also been found to be highly effective (Example 8). Indeed, ultrasonic treatment during the crystallisation process itself also accomlishes a similar end result (Example 9). The duration of the ultrasonic treatment, and the frequency and intensity of the radiation can be selected by those skilled in the art to achieve the desired end result. The crystal fracturing process can be coveniently followed by particle size analysis of samples periodically removed from the system. As can be seen from Fig 2, ultrasonic treatment causes cleavage of the needles perpendicular to the long axis, with a corresponding decrease in the length to breadth ratio. This can be seen in the particle size analysis as a decrease in the VMD from initial values in the range 100-250μm to values <100μm, most preferably in the range 20-60μm. It is to be noted that the crystal fracturing process is accompanied by an increase in the bulk density of the HNS, values in the range 0.8-0.95gcm^{3} being easily attained. Example 5 shows the typical changes in VMD and bulk density which occur during ultrasonic treatment.

Similar ultrasonic treatment of HNS I, whose crystals are plate-like, causes only small and somewhat unpredictable changes in VMD and bulk density (Examples 10 and 11). In addition, the dried product is strongly electrostatically charged and causes severe handling difficulties.

A complete characterisation of the product obtained by recrystallisation of HNS from N-methylpyrrolidone + toluene at 125°C, followed by ultrasonic treatment in 6% MeOH in H_2O, is shown in Table 1, together with the corresponding analyses of the starting HNS I and the specification for HNS II. It should be noted that the final product satisfies all the specification requirements for HNS II. In addition, measurements on pressed samples of this material (1500kgcm^{2}, density 1.64gcm^{3}) after being heated at 232°C for 200h, showed a weight loss of 1.05%, density 1.61gcm^{3}, and no significant change in the detonation velocity (6 917ms^{1} after heat treatment ; control 7 029ms^{1}).

Example 1

HNS (200g) was recrystallised by dissolution in N-methylpyrrolidone (1125ml) at 125°C and then slow cooling to 10°C. The solid was filtered off, was washed with MeOH (2X) and 3%MeOH in H_2O (3X), and then dried. Yield: 147g (73.5%). Bulk density 0.42gcm^{3}, VMD 251μm. Vacuum test (260°C): 0.44mlg^{1} after 20min, 0.27mlg^{1}h^{1} after 2h.

Example 2

HNS (400g) was dissolved in N-methylpyrrolidone (2250ml) at 125°C. PhCl (2250ml) was then added with mechanical stirring during 50min while keeping the temperature at 125°C. The mixture was cooled in air to 65°C and then in ice/water to 10°C. The solid was filtered off, was washed with MeOH (2X) and 3% MeOH in H_2O (3X), and then dried. Yield:342g (85.5%). Bulk density 0.48gcm^{3}, VMD 184μm. Vacuum test (260°C): 0.38mlg^{1} after 20min, 0.29 mlg^{1}h^{1} after 2h.

Example 3

HNS (400g) was recrystallised from N-methylpyrrolidone and PhCl as in Example 2, except that cooling from 125°C was with ice/water throughout. Yield: 340g (85%). Bulk density 0.44gcm^{3}, VMD 193μm. Vacuum test (260°C): 0.51mlg^{1} after 20min, 0.12mlg^{1}h^{1} after 2h.

Example 4

HNS (400g) was recrystallised as in Example 3, except that $PhCH_3$ was used instead of PhCl. Yield: 328g (82%). Bulk density 0.30gcm^{-3}, VMD 135µm. Vacuum test (260°C): 0.51mlg^{-1} after 20min, 0.10$mlg^{-1}h^{-1}$ after 2h.

Example 5

Samples of recrystallised HNS (from N-methylpyrrolidone and $PhCH_3$ or PhCl) with known bulk densities were suspended in 6% MeOH in H_2O (3500ml solvent/300g HNS) and treated ultrasonically with stirring. After treatment, the solid was filtered off and dried. Table 2 shows the changes in bulk density and VMD which were observed. All products exhibited excellent handling properties. Ultrasonic treatment was performed using an ultrasonic bath, type Sonorex RK106S supplied by Bandelin Electronic, West Germany, operating at 35kHz. The same ultrasonic bath was used in Examples 6-11.

Table 2

Duration of treatment/h	Bulk density/gcm^{-3} Initial	Final	VMD/µm Initial	Final
2	0.30	0.89	135	28
1	0.44	0.88	193	30
1	0.50	0.94	-	38
2	0.51	0.96	-	48
1	0.56	0.86	-	56
0.5	0.60	0.90	-	54
1	0.63	0.95	-	47

Example 6

HNS (27g) was recrystallised from DMF and PhCl at 100°C and then cooled to 10°C. The solid was filtered off, was washed with 3% MeOH in H_2O (3X) and then dispersed in 3% MeOH in H_2O (600ml). The suspension was treated ultrasonically with stirring during 45min. Some solid floated on the surface during the ultrasonic treatment. The solid was filtered off and dried. Yield: 21g (78%). Bulk density 0.85 gcm^{-3}, VMD 21µm.

Example 7

HNS (27g) was treated as in Example 6 except that 50% MeOH-H_2O (600ml) was used in the ultrasonic treatment. No solid remained floating on the surface. After 45min treatment, the solid was filtered off (filtration was very much slower than in Example 6) and dried. Yield: 21g (78%). Bulk density 0.85gcm^{-3}, VMD 25µm.

Example 8

HNS (304g) was dissolved in N-methylpyrrolidone (1750ml) at 125°C. PhCl (1750ml) was then added with mechanical stirring during 50min while keeping the temperature at ca 125°C. After cooling, the suspension was transfered to a beaker placed in an ultrasonic bath and treated ultrasonically with mechanical stirring during 2h. The solid was filtered off, was washed with MeOH (2X) and 3% MeOH in H_2O (3X) and then dried. Yield: 264g (87%). Bulk density 0.95gcm^{-3}, VMD 44µm.

Example 9

HNS (9.0g) was dissolved in DMF (150ml) at 100°C. The recrystallisation flask was then transfered to an ultrasonic bath filled with boiling water. With moderate mechanical stirring of the solution, PhCl (150ml) was added during 35min. The temperature at the end of the addition was 65°C. The ultrasonic bath was operated throughout the addition and subsequent cooling to 20°C. The solid was filtered off, was washed with water and then dried. Yield: 8.1g (90%). Bulk density 0.78gcm ^{3}, VMD 31µm.

Example 10

HNS I (110g), which had bulk density 0.42gcm ^{3} and VMD 47µm, was suspended in 3% MeOH in H_2O (3000ml) and treated ultrasonically during 1.5h. The solid was then filtered off and dried. Yield:106g. Bulk density 0.47gcm ^{3}, VMD 10µm.

Example 11

HNS I was treated as in Example 10, but only for 5min. The product had bulk density 0.37gcm ^{3} and VMD 24µm.

The products from Examples 10 and 11 were difficult to filter off and caused severe electrostatic problems when dry.

Claims

1. A method for the production of a 2,2',4,4',6,6'-hexanitrostilbene (HNS) with specified purity from a less pure raw-product, generally referred to as HNS I, comprising recrystallisation of the above raw-product from N-methylpyrrolidone (1-methyl-2-pyrrolidone).

2. A method for the production of a 2,2',4,4',6,6'-hexanitrostilbene with specified purity and a bulk density > 0.45gcm ^{3} from a less pure raw-product with lower bulk density, generally referred to as HNS I, comprising recrystallisation of the raw-product from a solvent having the ability to dissolve 2,2',4,4',6,6'-hexanitrostilbene and subsequent ultrasonic treatment of the resulting crystals.

3. A method for the production of a 2,2',4,4',6,6'-hexanitrostilbene (HNS) with specified purity and a bulk density > 0.45gcm ^{3}, generally referred to as HNS II, from a less pure raw-product with lower bulk density, generally referred to as HNS I, comprising dissolution of the raw-product (HNS I) in a solvent having the ability to dissolve 2,2',4,4',6,6'-hexanitrostilene (HNS) followed by separation of the purer product in the form of new crystals, which are then ultrasonically treated in order to decrease the length to bredth ratio of the crystals and to increase the bulk density of the resulting product.

4. A method according to claim 3 in which, during the recrystallisation process, the raw-product (HNS I) is dissolved in N-methylpyrrolidone (1-methyl-2-pyrrolidone) and from which solvent the purer product crystallises out through lowering of the capacity of the N-methylpyrrolidone to dissolve HNS.

5. A method according to claim 4 in which the separation of new crystals during the recrystallisation process is aided by lowering the temperature of the solution.

6. A method according to claim 4 in which the separation of new crystals during the recrystallisation process is aided by the addition of a second solvent having a lower capacity to dissolve HNS than N-methylpyrrolidone.

7. A method according to claim 6 in which either toluene or chlorobenzene is added in order to reduce the capacity of N-methylpyrrolidone to dissolve HNS.

8. A method according to one or more of claims 3-7 in which the recrystallised product is dispersed or suspended in a chemically inert liquid during the ultrasonic treatment.

9. A method according to claim 8 in which the ultrasonic treatment is performed either in an ultrasonic bath or in a vessel fitted with a submersible ultrasonic generator.

10. A method according to claim 8 in which the ultrasonic treatment is performed in a flow-through ultrasonic cell.

11. A method according to one or more of the above claims in which the recrystallised product is ultrasonically treated as a dispersion or suspension in an inert liquid system which consists partially or completely of water.

12. A method according to one or more of claims 2-10 in which the recrystallised product is ultrasonically treated in the mother liquor from which the product has crystallised.

13. A method according to claim 12 in which ultrasonic treatment is performed simultaneously with the crystallisation process.

14. A method according to one or more of claims 2-13 in which ultrasonic treatment is used to improve the flow and handling characteristics of the solid HNS crystals.

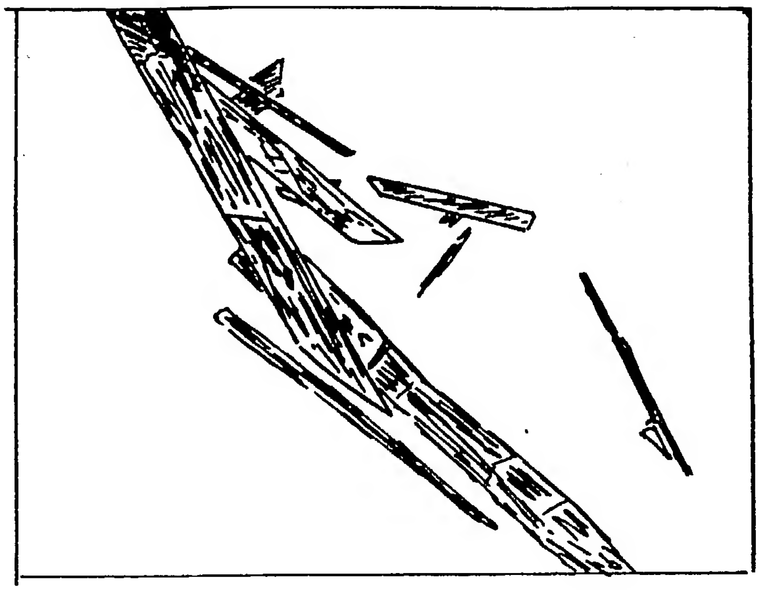

Fig. 1

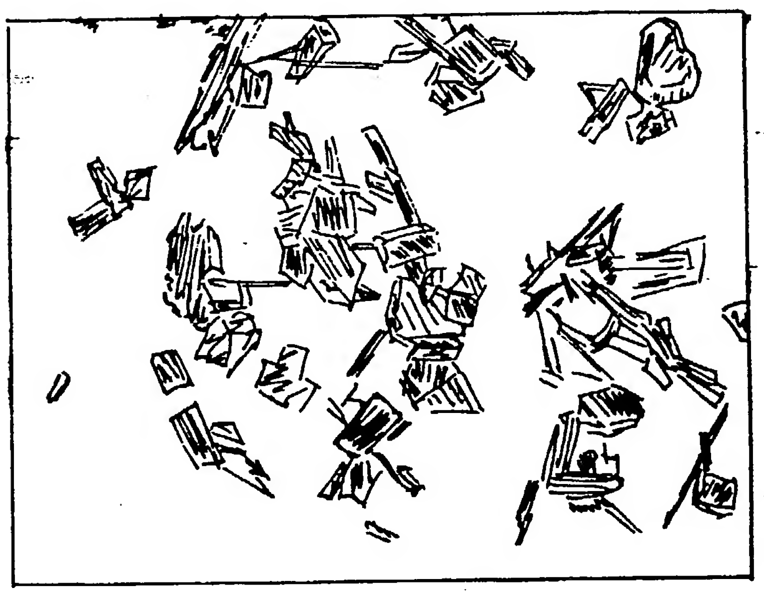

Fig. 2